

Article

Enteromorpha compressa Macroalgal Biomass Nanoparticles as Eco-Friendly Biosorbents for the Efficient Removal of Harmful Metals from Aqueous Solutions

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Abstract: This study focuses on the biosorption of harmful metals from aqueous solutions using *Enteromorpha compressa* macroalgal biomass nanoparticles as the biosorbent. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction analysis (XRD) were employed to characterize the biosorbent. The effects of pH, initial metal ion concentration, biosorbent dosage, and contact time on the biosorption process were investigated. The maximum biosorption capacity for metals was observed at a pH of 5.0. The experimental equilibrium data were analyzed using three-parameter isotherm models, namely Freundlich, Temkin, and Langmuir equations, which provided better fits for the equilibrium data. A contact time of approximately 120 min was required to achieve biosorption equilibrium for various initial metal concentrations. Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) demonstrated distinct maximum biosorption capacities of 24.99375 mg/g, 25.06894 mg/g, 24.55796 mg/g, 24.97502 mg/g, and 25.3936 mg/g, respectively. Different kinetic models were applied to fit the kinetic data, including intraparticle diffusion, pseudo-second-order, and pseudo-first-order versions. The pseudo-second-order model showed good agreement with the experimental results, indicating its suitability for describing the kinetics of the biosorption process. Based on these findings, it can be stated that *E. compressa* nanoparticle demonstrates potential as an effective biosorbent for removing targeted metals from water.

Keywords: *Enteromorpha compressa*; nanoparticles; biosorption; kinetics; heavy metals; isotherm



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1. Introduction

Heavy metal pollution, resulting from industrial activities, has significant consequences for environmental quality, affecting air, water, and soil and leading to the degradation of natural resources [1]. Among toxic pollutants, metallic impurities, particularly heavy metals, are of utmost concern due to their extreme toxicity, resistance to degradation, and ability to accumulate in the environment, leading to them being classified as high-risk pollutants [2].

Cadmium (Cd) and zinc (Zn) are notable contributors among the various heavy metals of concern. These metals are released into the environment as byproducts of industrial operations like galvanizing, refining, metallurgical processes, and electrochemical activities. The Environmental Protection Agency (EPA) has established specific acceptable concentrations for Cd and Zn in drinking water, which are 0.05 parts per million (ppm) and 5 ppm, respectively [3].

The discharge of untreated industrial wastewater into water bodies has become a pressing environmental issue [4]. This wastewater originates from diverse sources, such

as tanneries, pharmaceuticals, pesticides, rubber production, and plastics industries, as well as from lumber and timber product manufacturing [5,6]. Unfortunately, adequate treatment measures are often lacking for such wastewater.

By 2050, the effluents of certain chemicals are projected to increase significantly, ranging from 150% to 180%. This will pose substantial challenges to water quality. Among the contributing factors to water pollution are various chemicals utilized in agriculture, including herbicides, insecticides, fungicides, and others. The global usage of agricultural chemicals currently amounts to 2 million tons per year. There is a growing list of contaminants of concern, including novel pollutants such as pharmaceuticals, industrial chemicals, and nanomaterials. These pollutants are frequently detected at unexpectedly high concentrations, further emphasizing the need for effective water management strategies [7].

The significant quantity and high concentration of heavy metals in industrial wastewater pose considerable risks to both environmental and human health. Heavy metal concentrations in potable water and wastewater have consistently exceeded permissible limits in numerous nations [8].

The accumulation of heavy metals in the body, particularly through the food chain, makes humans and other animal predators susceptible to their toxic effects, leading to potential adverse health outcomes [9,10]. Moreover, heavy metals' long-lasting nature, high toxicity, and ability to accumulate in living organisms pose significant threats to the natural ecosystem, causing adverse effects on the ecological balance and risking non-targeted organisms.

To address the challenges associated with heavy metal removal from wastewater, various methods have been employed, including adsorption, chemical precipitation, membrane purification, ion exchange, and biological methods [11–13]. However, conventional processes often suffer from drawbacks such as high costs, energy intensity, limited removal efficiency, and the potential generation of secondary byproducts that impact the ecological system [14].

Given these challenges, there is a crucial need to develop basic, environmentally friendly techniques for heavy metal elimination from wastewater. Recent studies emphasize the importance of utilizing eco-friendly materials and basic compounds for heavy metal removal, offering promising prospects for efficient and environmentally conscious solutions [15,16].

Biosorption, a method involving the specific binding and concentration of heavy metals from diluted aqueous solutions using microbial detritus, holds significant promise for the removal of hazardous metals from natural waters and industrial wastewater [17].

Biosorption offers advantages such as the utilization of readily available and renewable biomaterials as sorbents, minimizing the need for costly and energy-intensive processes associated with conventional techniques [18]. Additionally, biosorption has shown potential for selective metal removal, making it suitable for the targeting of specific heavy metal contaminants. The large surface area, chemical composition, and functional groups of microbial detritus facilitate strong binding interactions with heavy metal ions, efficiently sequestering them and reducing their concentration in wastewater in order to meet regulatory standards [19].

Seaweeds, or marine macroalgae, are recognized as valuable biomass resources due to their effective metal removal capabilities [18,20]. These organisms contain diverse bioactive phytochemicals with active functional groups, such as carboxyl, phosphate, amine, and hydroxyl, that establish strong bonds with hazardous metals through negative charges [21]. Seaweed's phytochemical composition enables the formation of robust complexes with heavy metals, effectively sequestering them from the surrounding environment [22].

In our study, we specifically focus on *Enteromorpha compressa* macroalgal biomass nanoparticles. *Enteromorpha compressa* is a commonly available macroalga with distinct physical and chemical properties that make it well-suited for metal removal from aqueous solutions. Furthermore, its ability to be cultured commercially enhances its potential for large-scale applications [23].

The primary objective of this research endeavor was to thoroughly assess the effectiveness of *Enteromorpha compressa* biomass nanoparticles as eco-friendly biosorbents for removing harmful metals (cadmium, nickel, cobalt, lead, chromium, and copper) from an aqueous solution, considering a range of influential factors. These factors encompass agitation time, contact time, pH, biosorbent concentration, and the ratio of heavy metal ions. Thermodynamic, isothermal, and kinetic modeling techniques were employed to accomplish this. These modeling approaches enabled us to better understand the underlying mechanisms of metal adsorption by *Enteromorpha compressa* biomass nanoparticles and predict their performance under various conditions.

2. Materials and Methods

2.1. Preparation of Biosorbent

The biosorbent used in this study was prepared from freshly collected *Enteromorpha compressa* macroalgae samples obtained from the littoral area of the Red Sea in Egypt. The collected algae were rinsed thoroughly to remove impurities. Then, the purified biomass underwent solar drying for three days, followed by controlled drying at 50 °C for three days to obtain a desiccated sample. The desiccated sample was finely ground to achieve the desired particle size. The biosorbent material was stored at 4 °C for further use in the biosorption process.

2.2. Metal Solution Preparation

For this investigation, stock solutions containing metal ions at a concentration of 1000 mg L⁻¹ were used. Working solutions, with concentrations ranging from 5 to 100 mg L⁻¹, were prepared by diluting the stock solution. Analytical-grade standard chemical reagents from Sigma-Aldrich were used. To adjust the pH of the working solutions, NaOH or HCl solutions (0.1–1 M) were added after adding the biomass. The pH levels were measured using a pH instrument.

The metal ion concentrations in the solution were determined using inductively coupled plasma mass spectrometry (ICP-MS). This analytical technique accurately quantified the metal ions in the solution, providing valuable data for the study.

2.3. Biosorbent Characterization

Following the filtration of raw, metal-loaded biosorbent samples mixed with 100 mg L⁻¹ of metal ions, the samples were subjected to desiccation. These desiccated specimens were then analyzed using an FTIR spectrometer covering a wavelength range of 400–4000 cm⁻¹. The FTIR spectroscopic technique was employed to identify the active functional sites present on the surface of the biosorbent.

To gain further insights into the surface characteristics of the unloaded biomass, FTIR, XRD, and SEM techniques were employed. FTIR analysis allowed for the identification of functional groups on the surface of the biosorbent, while XRD analysis provided information about the crystallographic structure of the material. Additionally, SEM was utilized to observe and characterize the surface microstructure of the biomass cells.

2.4. Investigation of Metal Biosorption

The experiments on metal sorption were carried out in 250 mL beakers, each containing 50 mg of biosorbent material and 100 mL of synthetic metal solutions with a concentration of 100 mg/L. The purpose was to determine the optimal pH value and contact times for biosorption. The beakers were agitated at 150 rpm using a mechanical agitator for 180 min at a temperature of 25 °C. Subsequently, the biosorption solution was centrifuged at 5000 rpm for 5 min to separate the suspended particulates from the biomass material. To assess the impact of pH on the biosorption of metal ions, the experimental medium was adjusted to be either acidic, neutral, or alkaline, covering a pH range of 3–10. The residual metal ion concentrations were determined after the sorption experiment using 50 mg of various biomass samples with initial metal ion concentrations of 100 mg/L.

Biosorption experiments were conducted at different time intervals (0, 10, 20, 30, 40, 60, 120, and 180 min) using 50 mg of various biomass materials and an initial metal concentration of 100 mg/L. This was performed to investigate the effect of contact time on biosorption. To examine the biosorption isotherms, the effects of various metal concentrations were investigated, using 100 mg of different biomass materials in solutions with initial metal ion concentrations of 100, 200, 300, 400, and 500 mg/L. The impact of biomass quantities on the biosorption process was assessed by measuring residual metal ion concentrations, starting at 100 mg/L. Various amounts of biosorbent (50, 100, 150, 200, and 250 g) were utilized in the experiment to evaluate their influence on biosorption efficiency.

2.4.1. Kinetic and Adsorption Isotherm Investigations

The percentage of removal (% R), the quantity of metal adsorbed per unit mass of the algae at time t (q_t), and the quantity at equilibrium (q_e) were determined using the following equations (Equations (1)–(3)):

$$R(\%) = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

$$q_t = \frac{C_o - C_t}{m} \times V \quad (2)$$

$$q_e = \frac{C_e}{m} \times V \quad (3)$$

In the above equations, C_o , C_e , and C_t represent the initial, equilibrium, and remaining concentrations of metal in milligrams per liter at time t , respectively. m represents the mass of the biosorbent in grams, and V represents the volume of the solution being processed in liters.

For the analysis of equilibrium data, the Langmuir isotherm model (Equation (4)) and the Freundlich isotherm model (Equation (5)) were employed:

Langmuir equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}} \quad (4)$$

Freundlich equation:

$$\text{Log} Q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (5)$$

In the above equations, n is the Freundlich constant, q_0 (mg/g) represents the maximum biosorption capacity, b (L/mg) denotes the Langmuir constant, C_e (mg/L) signifies the metal concentration in solution at equilibrium, and K_F represents the distribution coefficient. The variables were determined by fitting the observed data into the Langmuir and Freundlich models.

The kinetic data for the research were obtained using the pseudo-first-order (PFO, Equation (6)) [24] and pseudo-second-order (PSO, Equation (7)) [25] models:

$$\text{Log} (q_e - q_t) = \text{Log} q_e - k_1 t \quad (6)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

In the above equations, q_t (mg/g) represents the quantity of heavy metals adsorbed at time t ; q_e (mg/g) denotes the quantity of heavy metals adsorbed at equilibrium; k_1 (1/min) signifies the rate constant for PFO; k_2 (g/mg) signifies the rate constant for PSO; a represents the initial rate constant in mg/g; and b represents the desorption constant.

Furthermore, the intraparticle diffusion (IPD, Equation (4)) [26] model was applied to the analysis of kinetic experimental data between 0 and 180 min:

$$q_e = k_{id} t^{1/2} + C \quad (8)$$

In the above equation, k_i represents the intraparticle diffusion rate constant ($\text{g}/\text{mg}/\text{h}^{0.5}$), and C signifies the intercept.

2.4.2. Regeneration and Desorption

The reusability of the biosorbent was investigated by researchers through the assessment of its performance with varying concentrations of hydrochloric acid (HCl), ranging from 0.1 to 0.5 M. The iterative process of sorption and desorption was carried out to evaluate the effectiveness of the biosorbent in removing metals.

After five cycles of sorption–desorption, the amount of desorbed metal was quantitatively estimated. The desorption efficiency was calculated using Equation (9), which allowed for the determination of how effectively the biosorbent released the adsorbed metals during the desorption process.

$$\text{Desorption efficiency} = \frac{\text{Quantity of metals desorbed}}{\text{Quantity of metals adsorbed}} \times 100 \quad (9)$$

3. Results and Discussion

3.1. Biomass Characterization

3.1.1. Surface Morphology Assessment through SEM Analysis

Figure 1 provides a morphological characterization of *E. compressa* nanoparticle biomass through SEM analysis. The images unveil the captivating granular-shaped structure adorning the surface of *E. compressa* nanoparticle biomasses, providing valuable insights into the intricate surface morphology of biosorbents. This unique granular surface exhibits tremendous potential for creating expansive domains, primed and ready for efficient metal biosorption, as evidenced by its remarkable surface-to-volume ratio. The collective arrangement of these minuscule particles amplifies their biosorption capacity, giving rise to a significant number of apertures.

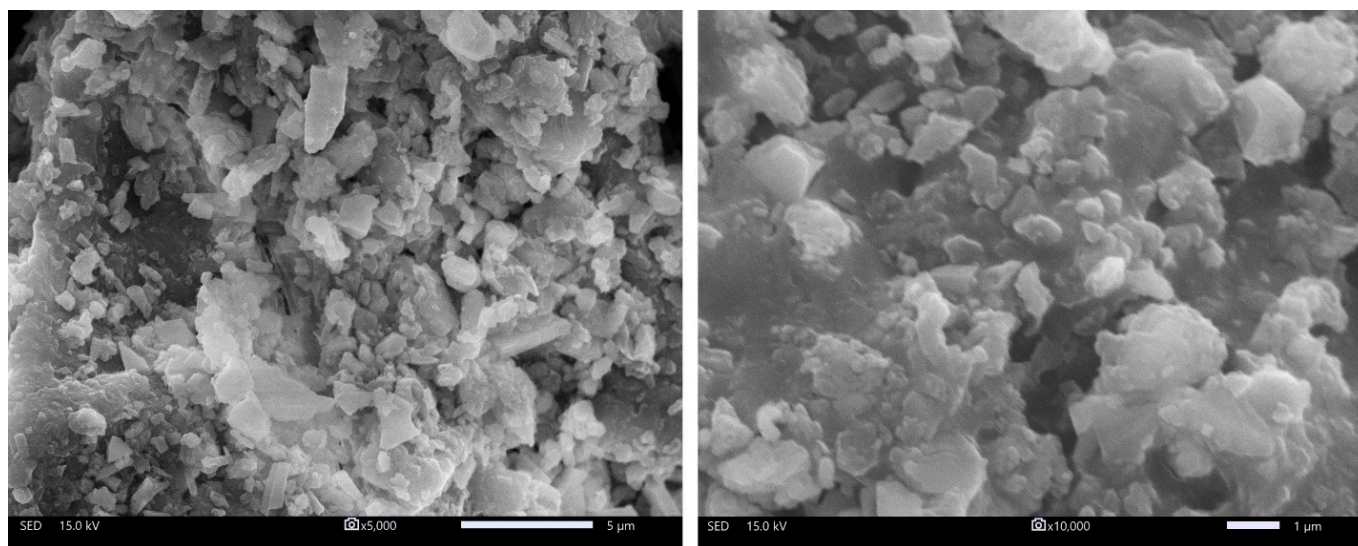


Figure 1. Scanning electron micrographs of *E. compressa* nanoparticle biomass.

Our observations revealed a fascinating range, spanning from 99 nm to 405 nm, with an average measurement score of 228.5 nm detected in particle size analysis. The biomass of *E. compressa* nanoparticles, with their delicate forms and intricate ridges, presents a heterogeneous surface landscape, inviting the exploration of metal ions. Its expansive surface area and distinctive grooved structure create an enticing habitat for these ions, offering ample opportunities for interactions with surface functional groups, unlocking a realm of captivating phenomena within the algal tissue.

The irregular and porous nature of the adsorbent areas contributes to an increased capacity for biosorption, a critical factor in enhancing absorption potential. SEM analysis confirms the biosorbent's strong affinity for metal uptake, attributable to its porous and uneven surfaces. The unloaded scanning electron microscopy image (Figure 1) reveals the presence of heterogeneous pores and their pre-existing structures, characterized by rough cavities; these play a pivotal role in the potential of these adsorbents [27].

Through these observations, we gain insights into how pollutant ions bind to the active sites on the surface of the *E. compressa* nanoparticle biomass, unraveling the intricate mechanisms of pollutant–ion interactions.

3.1.2. Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 2 exhibits the outcomes of FT-IR spectral analysis performed on *E. compressa* nanoparticles' biomass samples, both before and after metal sorption. In the biomass of untreated *E. compressa* nanoparticles, there is a strong and prominent peak at 3400.5 cm^{-1} [27]. This is typically attributed to N-H groups, which are likely cell wall components. Interestingly, this peak shifts to 3454.5 cm^{-1} following metal sorption. Additionally, a new peak emerges at 3344.57 cm^{-1} for the same functional group of N-H upon metal sorption. The well-known spectral band at 3223, detected in FTIR analysis, suggests the presence of the -OH functional group or hydrogen bonding. This distinctive peak is commonly associated with alcohols, phenols, and various organic acids that contain hydroxyl groups.

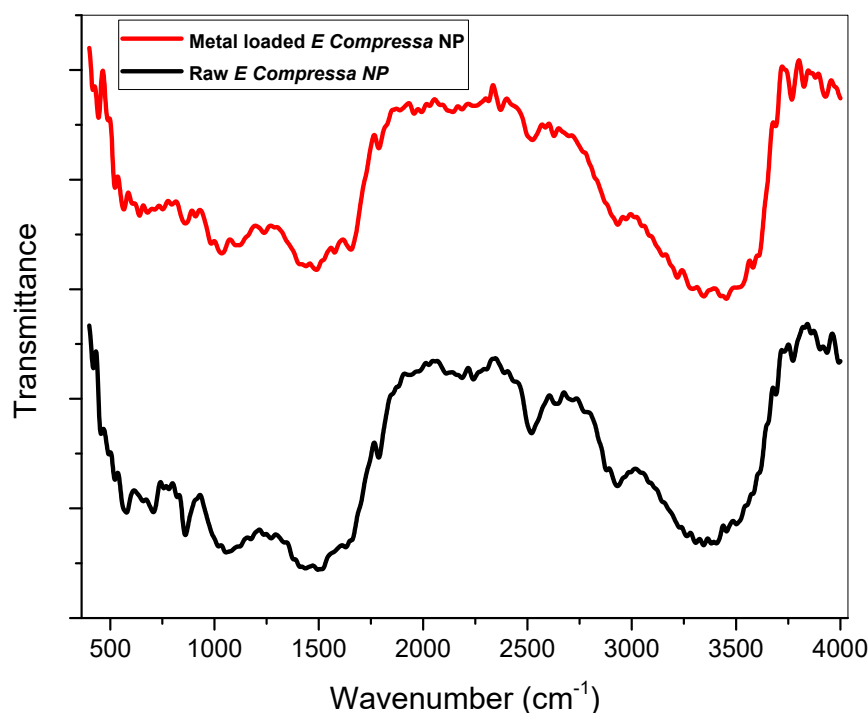


Figure 2. FTIR spectra of *E. compressa* nanoparticle biomass and metal-loaded *E. compressa*.

An intriguing finding is the peak shift to 3286.70 cm^{-1} after metal adsorption. This shift may indicate an interaction between the metal species and the hydroxyl groups in the sample or a change in the hydrogen bonding environment. The peak at 2927.4 cm^{-1} represents the symmetric C-H stretching vibrations of aliphatic functional groups in *E. compressa*. A peak at 2520 is typically associated with the $\text{-C}\equiv\text{C}$ functional group or carbon–carbon triple bonds. The new location of this peak at 2601 suggests a stronger binding of metal ions to the surface of *E. compressa*. The carbonyl group, previously characterized by a peak at 1645.28 cm^{-1} , shifts to 1649.16 cm^{-1} , indicating a change in its environment, possibly due to binding with metal ions. The transition from 1506.41 cm^{-1} to 1573.91 cm^{-1} , attributed to -CH stretching vibrations, also suggests a potential interaction between the functional group and metal

ions. Metal biosorption by *E. compressa* can lead to alterations in the C-O stretching vibration peak, shifting it from 1006.81 cm^{-1} to 1033.83 cm^{-1} . Additionally, the minor peak associated with S=O groups shifts from 867.97 cm^{-1} to 862.18 cm^{-1} due to metal biosorption by *E. compressa*.

3.1.3. X-ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a swift and prevalent analytical technique, primarily employed for the identification of crystalline materials and their respective phases.

The XRD profile of *E. compressa* nanoparticle biomass, captured in Figure 3, showcased distinct diffraction patterns, characterized by prominent peaks at 26.171° , 26.612° , 36.499° , and 30.909° . These significant peaks strongly suggest the presence of Dolomite, Aragonite, and Aluminum Neptunium, with no observation of these investigated metals within the *E. compressa* nanoparticle biomass.

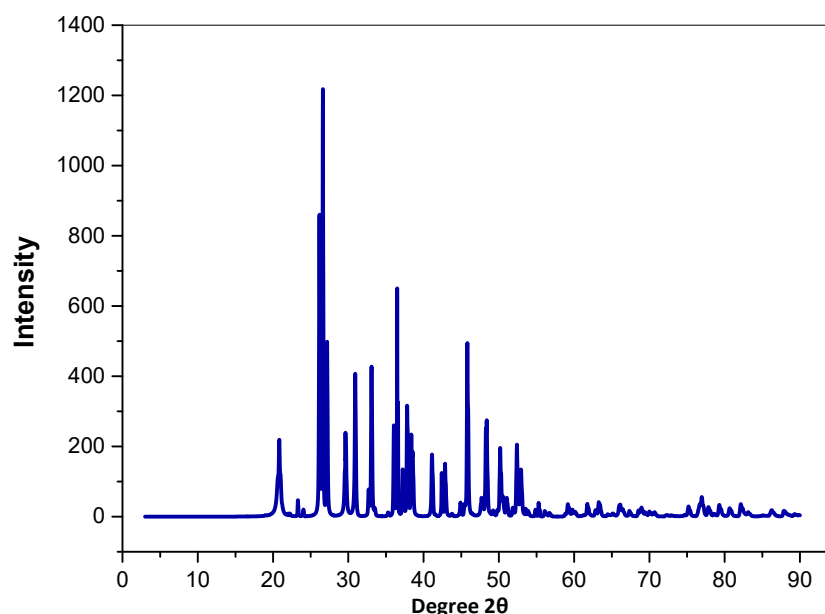


Figure 3. X-ray diffraction analysis of *E. compressa* nanoparticle biomass.

3.2. Investigating Biosorption

3.2.1. pH Effects on Metal Biosorption

The influence of initial pH on the biosorption efficiency of *E. compressa* nanoparticle biomass regarding Cr, Co, Ni, Cu, and Cd is illustrated in Figure 4. The results reveal a gradual increase in the adsorption capacity (q_e) of the tested metals with rising pH, peaking at pH 5, followed by a decline at higher pH values. At pH 5, *E. compressa* nanoparticle biomass demonstrates adsorption capacities of 24.98569 mg/g for Cr, 24.98888 mg/g for Co, 24.96921 mg/g for Ni, 24.96042 mg/g for Cu, and 24.99274 mg/g for Cd. The correlation between metal cation biosorption and solution pH can be attributed to protonation or deprotonation processes, occurring at the surface of the biosorbent.

Under extremely low-pH conditions (acidic), cation biosorption is hindered due to competition for functional sites between hydronium ions (H^+) and investigated metal ions. This leads to the formation of bonds between positive hydronium ions and ligands on the cell wall [28,29]. However, as the pH increases, more ligands become available, increasing the presence of negatively charged deprotonated active sites and facilitating cation uptake [30]. Conversely, when the pH surpasses 7, the biosorption efficiency diminishes due to the formation of solid-phase hydroxide complexes in the medium, leading to precipitation [29,30]. Based on our findings, all experiments were conducted at the optimal pH range of approximately 5–6 for the tested metal solutions.

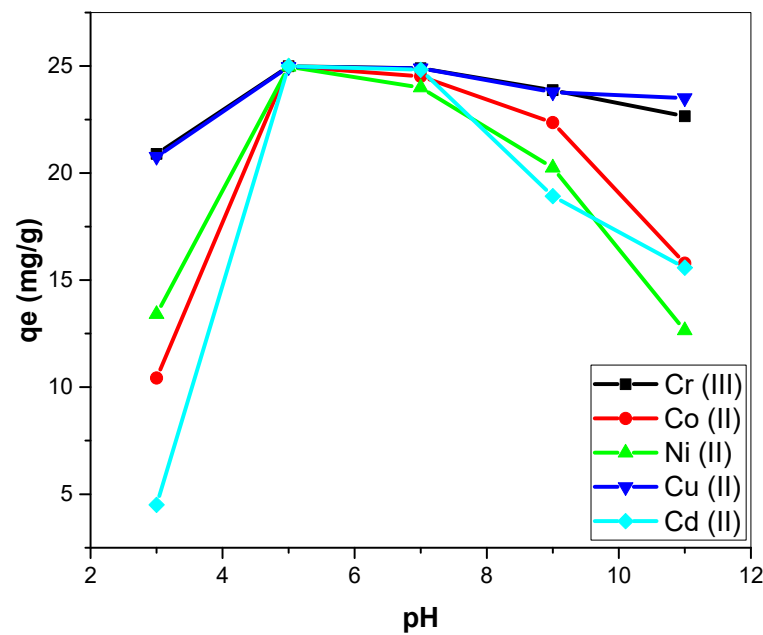


Figure 4. Influence of pH on the metal biosorption capacities of *E. compressa* biomass (m: 50 mg; C: 100 mg/L, and t: 120 min).

3.2.2. Implications of Biosorbent Dosage

As the dosage of *E. compressa* nanoparticle biomass increased from 10 mg to 50 mg, a slight increase in adsorption capacity was observed, ranging from 20.99698, 22.47292, 21.84532, 20.99609, and 20.27928 to 24.99174, 24.41123, 23.97129, 24.9786, and 24.92985 (Figure 5). However, no further changes in adsorption capacity were observed beyond a dosage of 50 mg. The doses of the adsorbent (50 mg) enhance the permeability of metals, resulting in increased adsorption capacity due to a larger surface area and greater availability of active sites [31]. However, within the dosage range of 50 mg to 250 mg, adsorption remains constant as the available active sites become saturated [32]. Therefore, a maximum effective dosage of 50 mg of *E. compressa* was established.

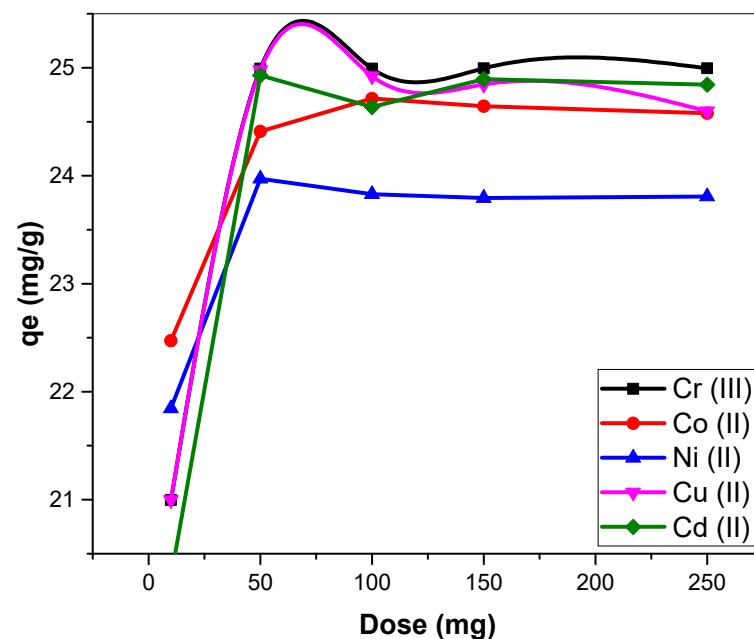


Figure 5. Influence of biosorbent dose on the metal biosorption capacities of *E. compressa* biomass (pH: 5; C: 100 mg/L, and t: 120 min).

This trend can be attributed to a decline in the effective surface area and biosorption sites of the biomass, which hinders the adsorption of metal ions. This decrease in surface area and biosorption sites is primarily caused by the aggregation of biosorbent material at higher concentrations [33].

3.2.3. Effect of Initial Metal Ion Concentration on Biosorption

The influence of metal ion concentration on biosorption was investigated, while keeping all other parameters constant. The results, presented in Figure 6, provide insights into the effect of heavy metal ion concentration on the sorption process. The findings unveiled that higher concentrations of heavy metals corresponded to improved adsorption capacities for the examined metals. Specifically, at a concentration of 500 mg/L, the *E. compressa* nanoparticle biomass exhibited adsorption capacities of 249.89343 mg/g for Cr, 222.38195 mg/g for Co, 197.696 mg/g for Ni, 249.86983 mg/g for Cu, and 176.4617 mg/g for Cd.

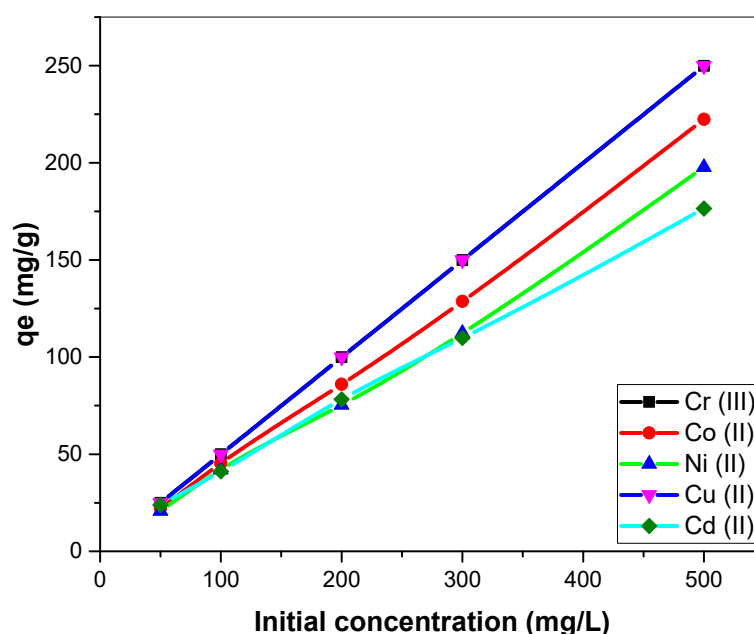


Figure 6. Influence of initial concentration on metal biosorption capacities of *E. compressa* nanoparticle biomass (pH: 5; m: 50 mg, and t: 120 min).

The presence of unoccupied binding sites played a crucial role in facilitating the highest possible biosorption of heavy metals, elucidating the observed sorption behavior. The treated sorbent material demonstrated the enhanced biosorption of heavy metals, which could be attributed to the dynamic force generated by the initial metal concentration. This force effectively overcame the mass transfer resistance between the solid material and the aqueous medium [22,30].

3.2.4. Influence of Reaction Time on Metal Biosorption

Figure 7 depicts the biosorption capacity of *E. compressa* biomass nanoparticles for removing Cr, Co, Ni, Cu, and Cd over time. The initial stages of the biosorption process exhibited a rapid rate of adsorption capacity. Within the first 40 min, approximately 24.99127 and 24.8836 of Cr and Cu ions, respectively, were biosorbed. Similarly, within the first 20 min, the adsorption capacity reached 22.67937, 21.5234, and 22.64609 for Co, Ni, and Cd, respectively.

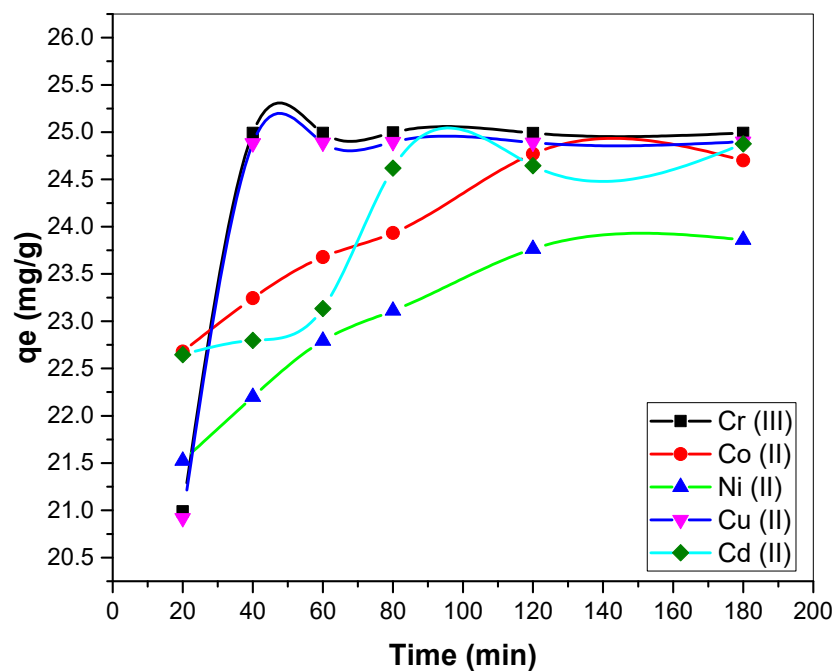


Figure 7. Influence of contact time on the metal biosorption capacities of *E. compressa* biomass (Experimental conditions: temperature: 25 °C; pH: 5; volume: 100 mL; initial mass: 50 mg).

The biosorption process continued to progress until it reached its maximum equilibrium stage after 120 min. At this point, the biosorption rate remained relatively constant, indicating no significant further changes in the biosorption process beyond the equilibrium stage. The rapid adsorption capacity observed during the initial stages highlights the efficiency of *E. compressa* biomass nanoparticles as biosorbents for removing Cr, Co, Ni, Cu, and Cd. Understanding the effect of contact time on biosorption can help to optimize the design and operation of biosorption processes in order to achieve efficient metal removal.

The rapid adsorption rate observed during the initial phase can be attributed to the abundance of the vacant surface groups available for binding. However, the occupation of residual unoccupied sites becomes challenging due to the repulsive forces between metal ions present in the solid biomass material and the contaminated aqueous solution [22,34,35]. The practical significance of the efficient removal observed in this study highlights this technique's potential application as an effective method in operational wastewater treatment facilities.

3.3. Biosorption Isotherm Models

Three isothermal models, namely the Langmuir, Freundlich, and Temkin models, were employed to evaluate the biosorption performance and equilibrium data of the investigated metals on *E. compressa* biomass nanoparticles. The experiments were conducted under specific conditions, including a pH of 5, a duration of 120 min, an algal dosage of 0.05 g at room temperature, and a stirring rate of 120 rpm. The linear isotherm equations used for the aforementioned models were found to be favorable for the initial metal concentrations of 100, 200, 300, 400, and 500 mg/L.

Table 1 presents the equilibrium parameters obtained by fitting the Freundlich and Langmuir models to the experimental data. The high correlation coefficients ($R^2 = 0.98$ for Ni, $R^2 = 0.96$ for Co, $R^2 = 0.99$ for Cd, $R^2 = 0.96$ for Cr, and $R^2 = 0.7$ for Cu) and good fit (Figure 8a,b) with the biosorption equilibrium data (Langmuir model) indicate that the biosorption process is homogeneous, suggesting a uniform biomass surface. The results from the Langmuir correlation test are higher than those from the Freundlich test (R^2) (Figure 8a,b). However, the Freundlich isotherm fails to adequately explain the biosorption

of metals onto *E. compressa* biomass nanoparticles, as indicated by the computed R^2 values shown in this investigation.

In Table 1, the maximal biosorption capacities (q_m) for metals by *E. compressa* biomass nanoparticles were determined to be 249.1901 mg/g for Cr, 217.5668 mg/g for Co, 201.6129 mg/g for Ni, 201.6129 mg/g for Cu, and 172.4138 mg/g for Cd. The calculated q_{max} values closely resembled the q_{max} values obtained from the experimental data. These values were comparable-to-higher than those reported in studies on the adsorption of metals by *Ulva lactuca* and *Saccharomyces cerevisiae* [36,37]. Analyzing the equilibrium data and establishing an equation is crucial for designing, optimizing, and comparing various sorbents under different operating conditions [38].

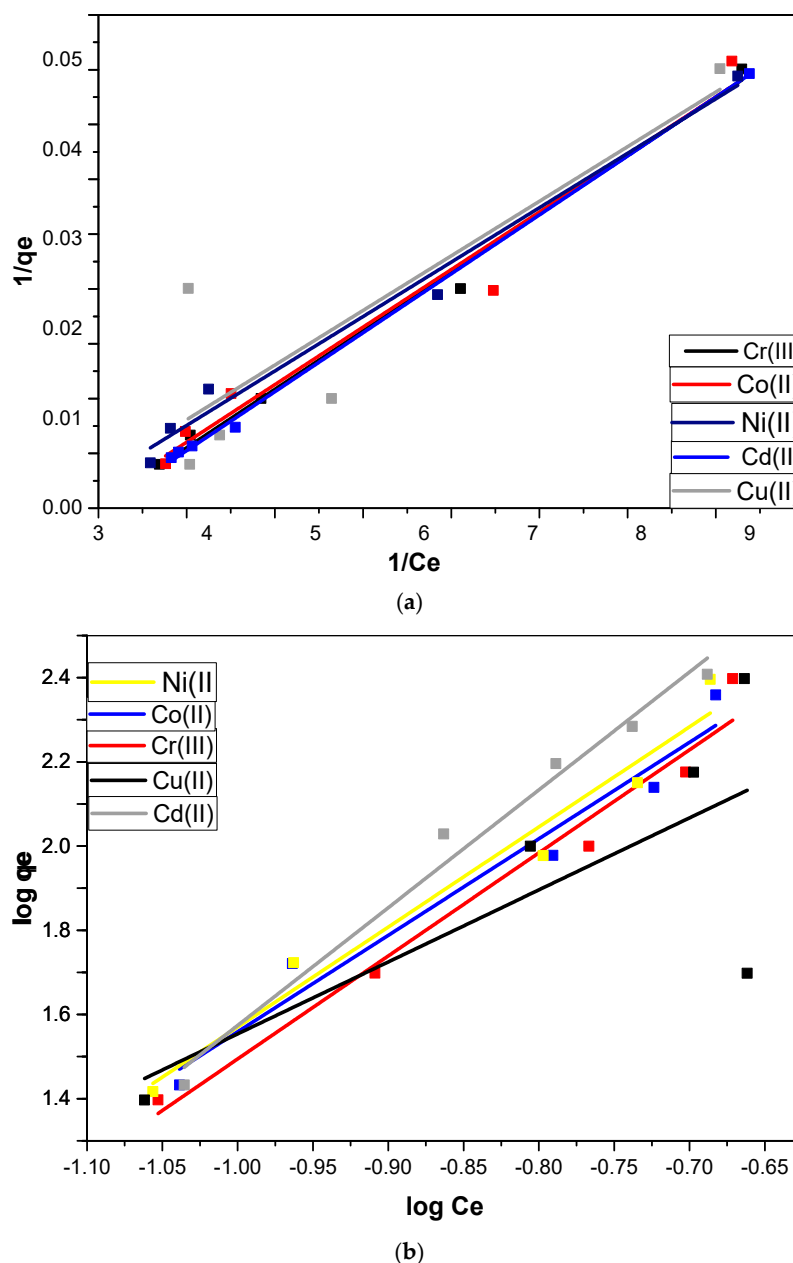
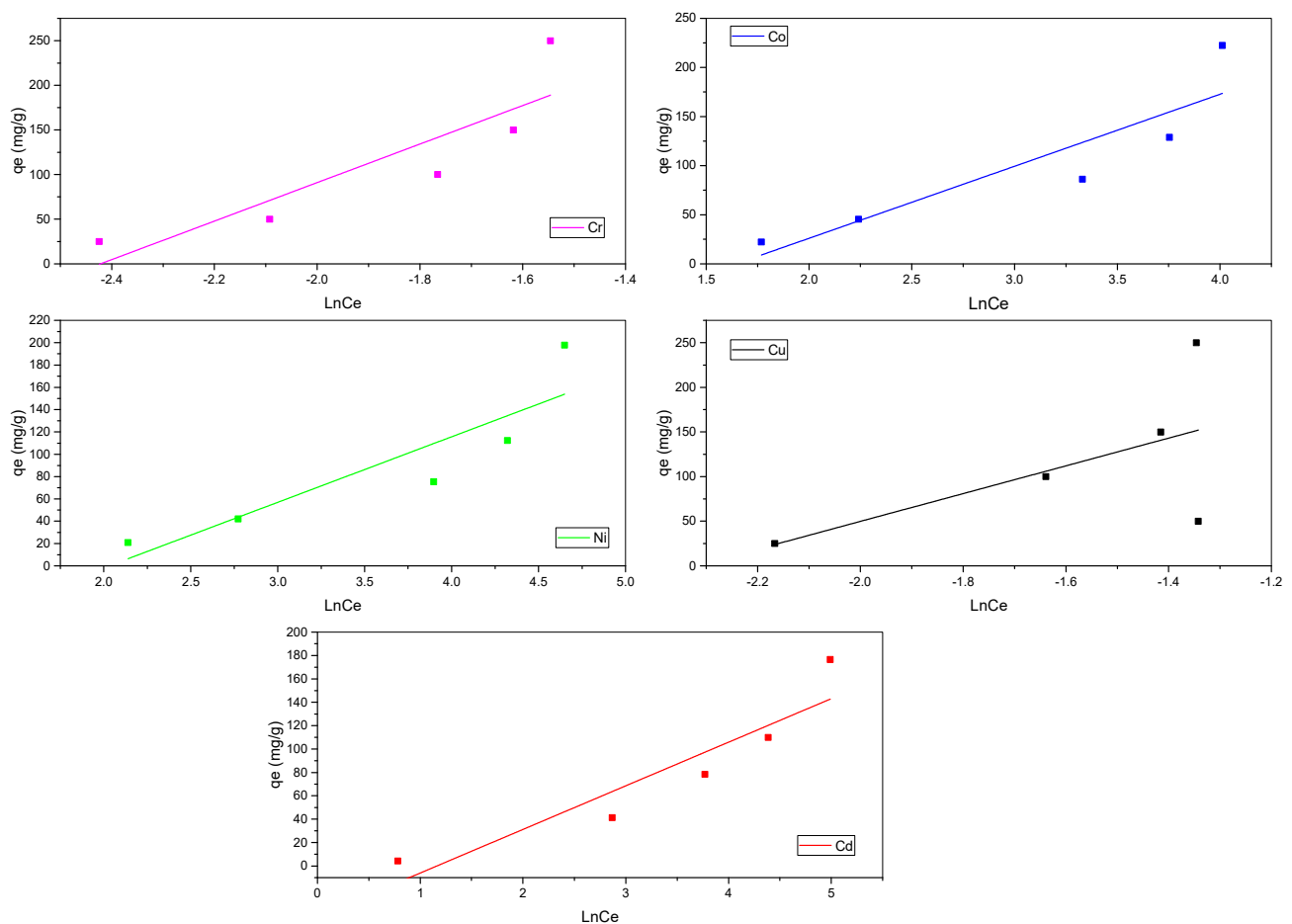


Figure 8. (a) Langmuir plot for the biosorption of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) ions onto *E. compressa* biomass nanoparticles (Experimental conditions: temperature: 25 °C; pH: 5; volume: 100 mL; initial mass: 50 mg). (b) Freundlich plot for the biosorption of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) ions onto *E. compressa* biomass nanoparticles. (Experimental conditions: temperature: 25 °C; pH: 5; volume: 100 mL; initial mass: 50 mg).

Table 1. Adsorption isotherms of onto *Enteromorpha compressa* biomass nanoparticles: computed parameters and analytical analysis.

Equilibrium Model	Parameters	Ni(II)	Co(II)	Cr(III)	Cu(II)	Cd(II)
Langmuir	qm ($\text{mg}\cdot\text{g}^{-1}$)	201.6129	217.5668	249.1901	201.6129	172.4138
	K_L ($\text{mg}\cdot\text{g}^{-1}$)	0.013279	0.018718	0.752908	0.661175	0.011124
	R_L ($\text{L}\cdot\text{mg}^{-1}$)	0.882773	0.842335	0.117246	0.131376	0.899898
	R^2	0.98	0.96	0.96	0.7	0.99
Freundlich	n	1.240187	1.102086	0.871293	1.91177	1.128643
	K_F ($\text{L}\cdot\text{mg}^{-1}$)	3.867319	4.87147	8.751047	1765.062	2.456009
	R^2	0.96	0.95	0.96	0.5	0.98
Temkin	B ($\text{J}\cdot\text{mol}^{-1}$)	58.74544	73.37301	215.8127	155.4976	37.29655
	K_T ($\text{L}\cdot\text{mg}^{-1}$)	0.131244724	0.192784789	11.265276	10.18093794	0.312696732
	R^2	0.73	0.8	0.7	0.3	0.8

Drawing upon the adsorbent–adsorbate interaction, the Temkin isotherm allows for the inference of a linear inverse relationship between biosorption heat and surface coverage [39]. The computed parameters of the Temkin isotherm model, namely AT and bT, are presented in Table 1. As stated by Rambabu [40], the bonding factor bT, derived from this isotherm model, indicates the physical nature of the observed biosorption. This indicates that no significant interaction occurs between the adsorbate molecules and the solid surface of the adsorbent (Figure 9).

**Figure 9.** Temkin plot for the biosorption of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) ions onto *E. compressa* biomass nanoparticles. (Experimental conditions: temperature: 25 °C; pH: 5; volume: 100 mL; initial mass: 50 mg).

3.3.1. Kinetic Models of Biosorption

The biosorption of metals onto *E. compressa* biomass nanoparticles is depicted in Figure 10 through the logarithmic plots of $\ln(q_e - q_t)$ versus t . The comparison presented in Table 2 reveals that the pseudo-first-order model exhibited a low coefficient of determination value in contrast to the other two kinetic models. Moreover, the significant disparity between the actual and computed uptake values further suggests that the biosorption kinetics do not conform to the pseudo-first-order model.

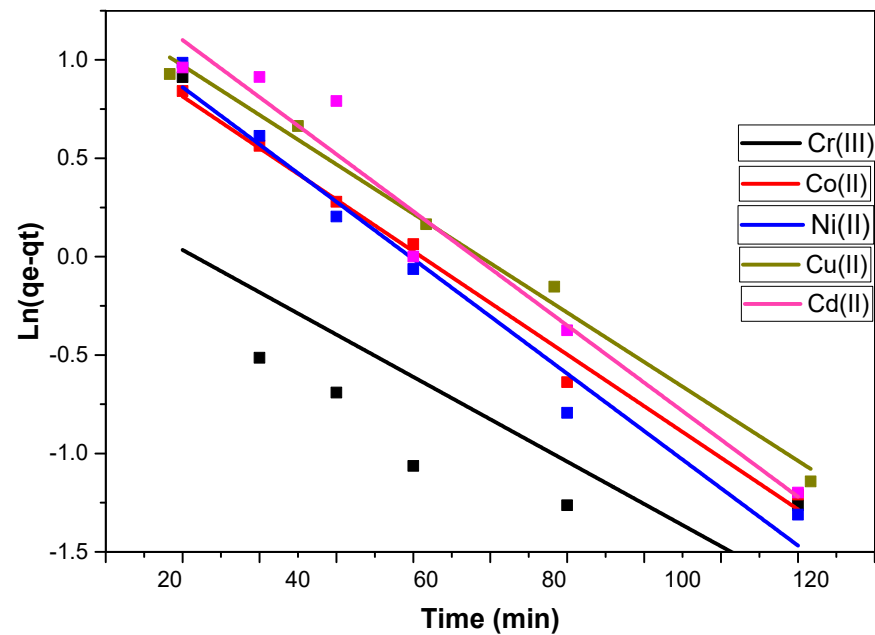


Figure 10. Pseudo-first-order kinetic analysis of biosorption for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) ions onto *E. compressa* biomass nanoparticles (Experimental conditions: temperature: 25 °C; pH: 5; volume: 100 mL; initial mass: 50 mg).

Table 2. Kinetic modeling of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) biosorption onto *E. compressa* nanoparticle biomass: computational parameters and analysis.

Kinetics Models	Variables	Parameters Unit	Cr(III)	Co(II)	Ni(II)	Cu(II)	Cd(II)
PFO	q_e	mg/g	0.010447	2.93366	3.830978	0.072258	4.227158
	R^2	-	0.56	0.988	0.97	0.987	0.95
PSO	q_e (calculated)	mg/g	24.99375	25.06894	24.55796	24.97502	25.3936
	R^2	-	0.999	0.999	0.999	0.999	0.999
IPD	K_{id}	((mg/g) min ^{-0.5})	0.000014	0.23106	0.29321	0.00417	0.26992
	c	-	24.98953	21.7876	20.37882	24.86572	21.37326
	R^2	-	0.44321	0.95863	0.96101	0.92284	0.80179

Figure 11 displays a linear relationship between t/q_t and t . As indicated in Table 2, the pseudo-second-order kinetics equation yielded a higher coefficient of determination value for the metals. Consequently, it can be inferred that the biosorption of the evaluated metals on *E. compressa* follows pseudo-second-order kinetics. This theory proposes that the rate-limiting step involves chemisorption, where *E. compressa* and metal ions engage in electron sharing and exchange [41]. These findings are consistent with the results obtained by Rangabhashiya [42].

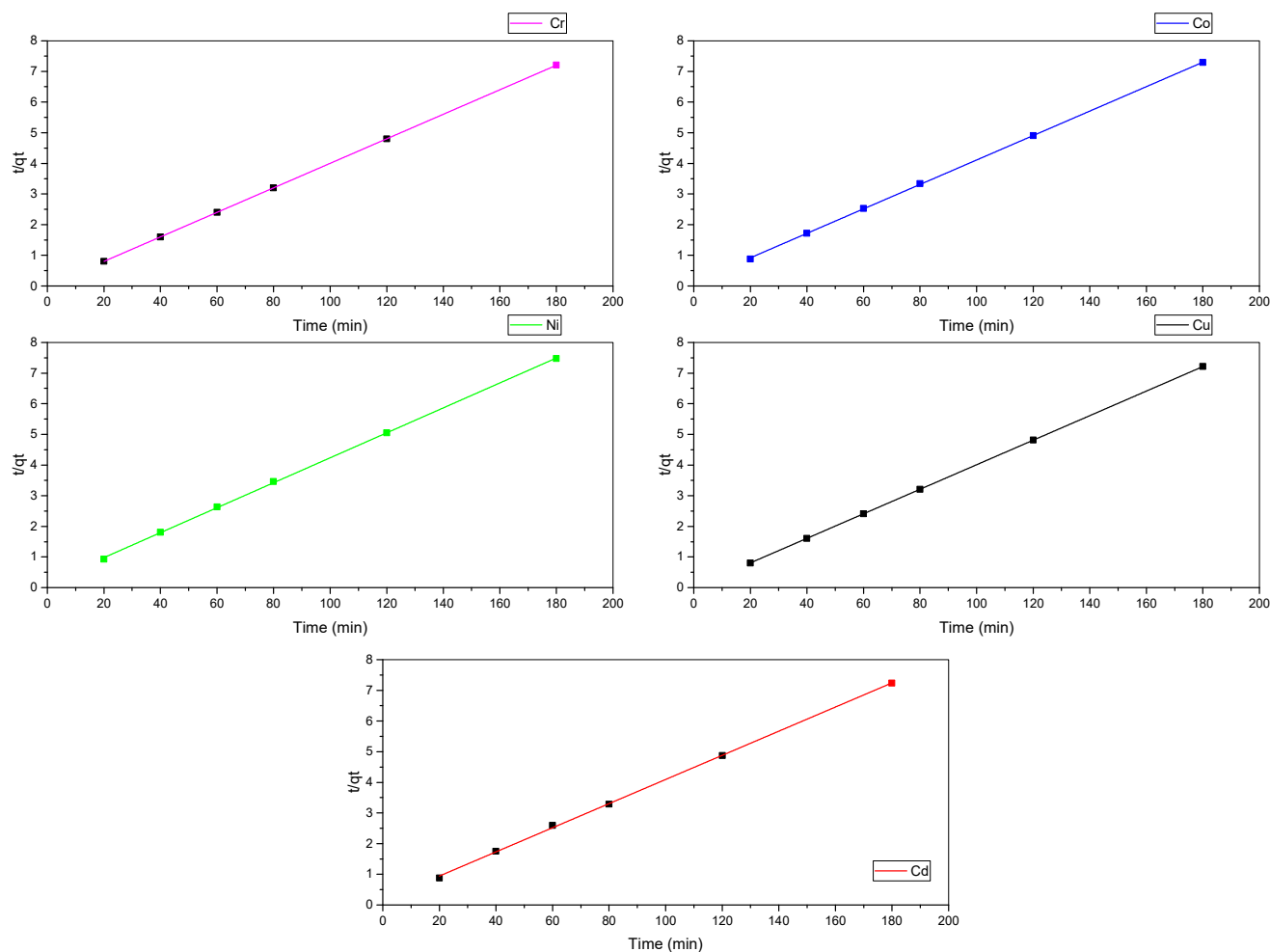


Figure 11. Pseudo-second-order kinetic analysis of biosorption for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) ions onto *E. compressa* nanoparticle biomass (Experimental conditions: temperature: 25 °C; pH: 5; volume: 100 mL; initial mass: 50 mg).

Table 2 presents the results of the rate constant and adsorption capacity calculations conducted using Origin software (Originpro 2016, 93E). The biosorption of metals by biomasses of *E. compressa* nanoparticles involves chemisorption, as indicated by the higher correlation coefficient values obtained from the PSO model [43]. The results of the PSO model's fit suggest that the removal mechanism is associated with the exchange of electrons or valence forces between bonds on the biomass surface and the pollutant.

The rate-determining step, often considered the slowest phase, can be identified among these processes. One of the processes involves solute ions moving from the bulk medium to the surface through the external film. Another process entails solute ions penetrating the interior layer of the sorbent from the surface. The third process involves solute ions attaching themselves to the micropores of the sorbent.

Figure 12 depicts the sorption rate, which initially exhibited a rapid increase and gradually decreased over time. Equilibrium was achieved in less than one hour, following a typical kinetic pattern where the sorbate molecules gradually occupied the available adsorption sites. Moreover, shorter time periods resulted in higher adsorption capacities, indicating that there were enhanced sorption capabilities within reduced time frames. These findings provide valuable insight into the kinetics of the biosorption process and highlight its potential for optimizing adsorption efficiency by manipulating the contact time.

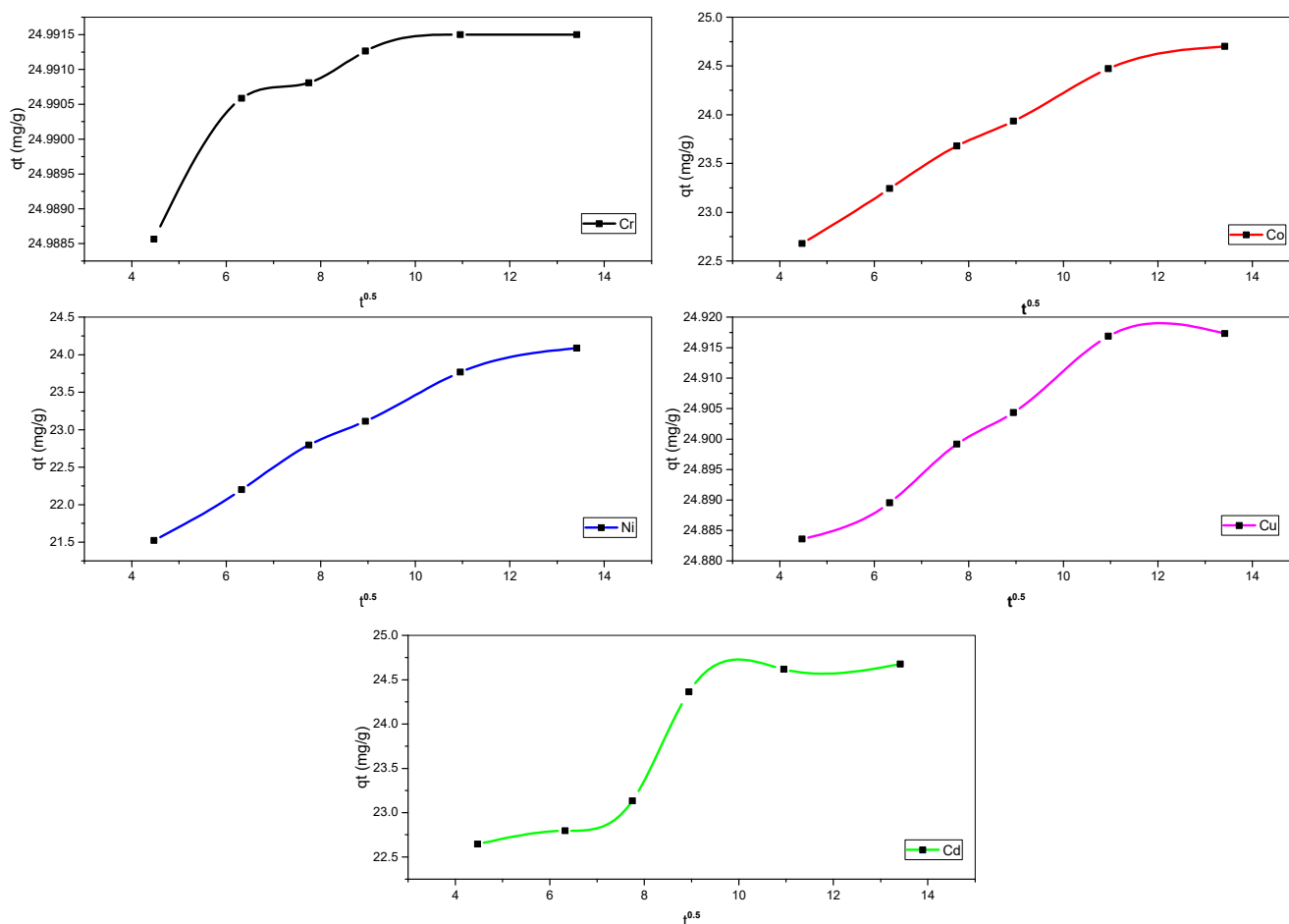


Figure 12. Intraparticle diffusion (IPD) kinetic analysis of biosorption for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) ions onto *E. compressa* biomass nanoparticles (Experimental conditions: temperature: 25 °C; pH: 5; volume: 100 mL; initial mass: 50 mg).

3.3.2. Adsorption Mechanism

Adsorption is a complex phenomenon that unfolds as metal ions bind to the surfaces of *E. compressa* biomass nanoparticles. Algal surfaces possess a diverse range of functional groups, including carboxyl, sulfate, amine, and hydroxyl, which serve as binding sites for metal ions [44]. Electrostatic interactions and hydrogen bonding contribute significantly to the binding process, orchestrating its harmonious progression. These functional groups confer a negative charge upon the surfaces of *E. compressa* biomass nanoparticles (Figure 13).

To enhance the adsorption process, the metals of interest become integrated into the structure of the adsorbent material. Metal ions form coordination bonds, seamlessly incorporating functional groups into the molecular framework. Complexation further enhances the accessibility of metal ion binding sites, while the porous nature of the adsorbent allows for the passage of metal ions [19]. The transfer of metal ions from the external solution to the interior is regulated by intraparticle diffusion. Equilibrium is achieved when the surface concentration of metal ions remains constant. The culmination of the adsorption process occurs when all available binding sites are occupied, leading to saturation [45,46]. Gaining a comprehensive understanding of these intricate processes is crucial for the development of effective strategies to remove these metals. Figure 13 provides a visual representation that elucidates the underlying mechanisms, guiding the way toward promising and practical solutions.

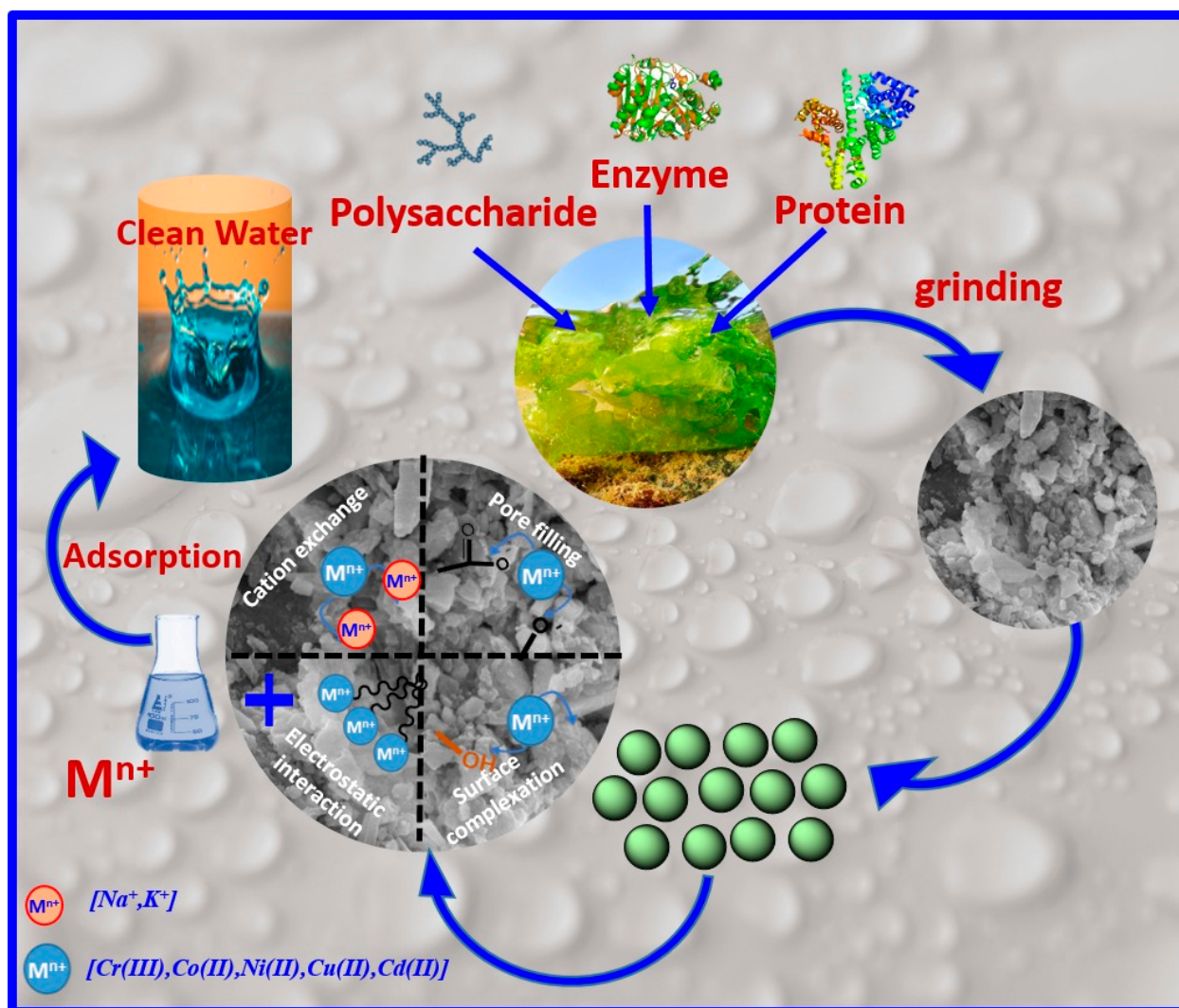


Figure 13. Schematic representation of the investigated adsorption process mechanism.

3.3.3. Desorption and Reusability of *E. compressa* Biomass Nanoparticles

To optimize the performance of algal biosorbents in water purification from metal contaminants, it is advisable to adopt a strategy of reusing and recycling them. This approach not only facilitates the widespread utilization of the technology but also leads to cost savings. The outcomes of a study investigating the desorption of investigated metal ions using varying concentrations of hydrochloric acid (HCl) are depicted in Figure 14. The results indicate that desorption remains effective up to an HCl concentration of 0.2 M.

Figure 14 demonstrates that, consistent with earlier research [46], the highest recoveries for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) were achieved with a 0.2 M HCl solution, yielding percentages of 87, 81, 93, 80, and 80, respectively. During the recycling process, when the biosorbent was reused five times, Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) were extracted from the biomass using 0.2 M HCl. The first two cycles exhibited adsorption efficiencies of over 88%, 85%, 77%, 88%, and 76% for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II), respectively.

The decline in biosorption effectiveness with the increasing cycle count can possibly be attributed to the concurrent loss of biomass. Jayakumar et al. [47] also observed that the acid has the potential to deactivate surface active sites, thereby reducing the removal efficiency. The findings highlight the suitability of the *E. compressa* nanoparticle biomass as a reusable biosorbent, demonstrating favorable efficiency for up to five cycles.

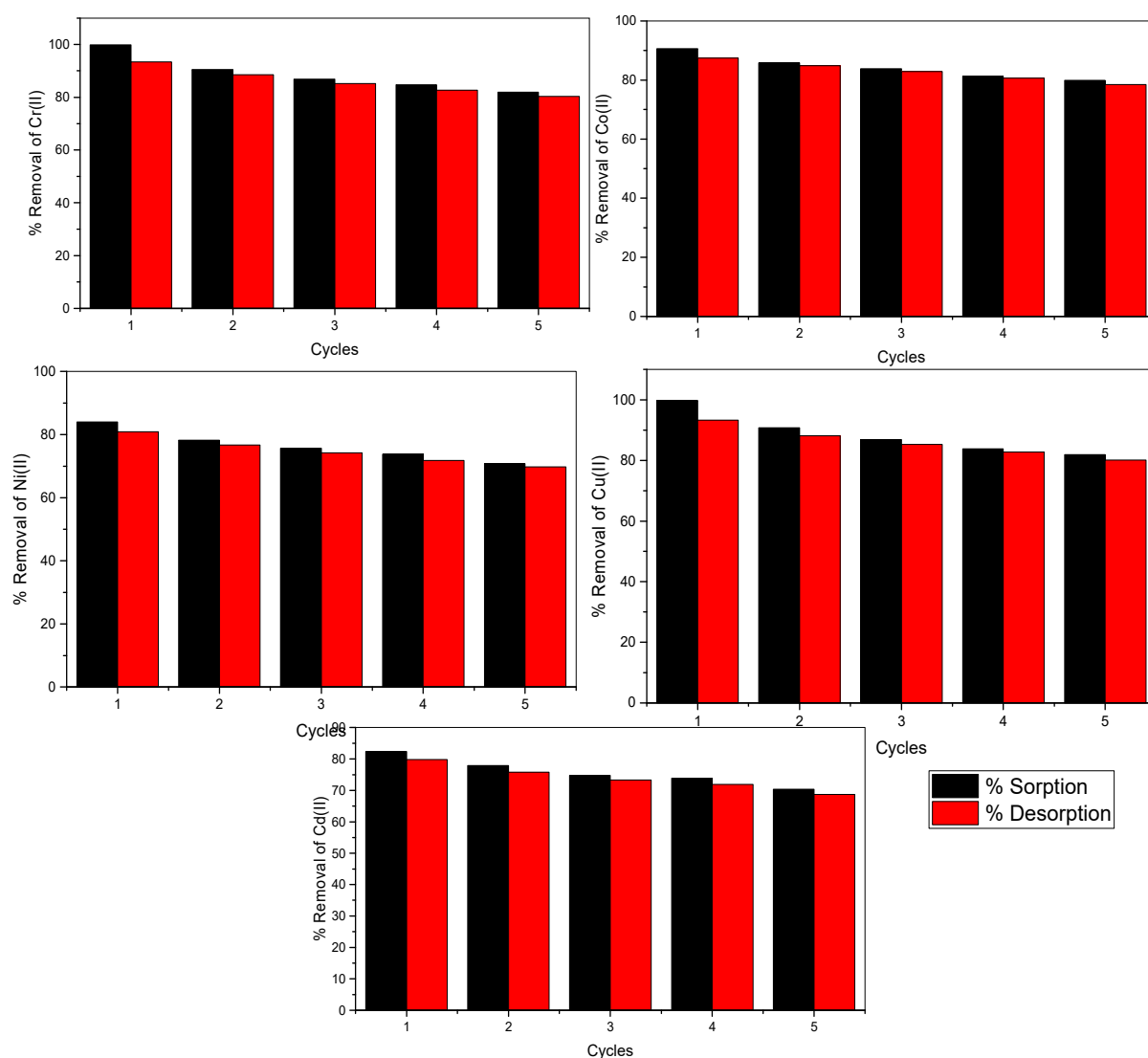


Figure 14. Sorption–desorption efficiencies of Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) for *E. compressa* nanoparticle biomass.

In comparison with the majority of the listed adsorbents, the *E. compressa* nanoparticle biomass exhibits superior biosorption capacity for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) (Table 3). The biosorption ability varies depending on factors such as the initial concentration of the adsorbate, the surface modification extent, and the specific properties of the adsorbent. Nevertheless, notable attention should be given to the promising capabilities of *E. compressa* nanoparticle biomass to effectively extract these detrimental metal ions from water sources.

This observation emphasizes the enhanced biosorption potential of *E. compressa* nanoparticle biomass when compared to other adsorbents. The efficacy of this algal species in capturing Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) is particularly noteworthy, underscoring its suitability for water remediation applications. The varying factors influencing biosorption performance highlight the importance of considering optimal conditions and tailored approaches in order to maximize the extraction efficiency of these harmful metal ions.

Table 3. Comparative analysis of adsorption capacities of *E. compressa* nanoparticle biomass for Cr(III), Co(II), Ni(II), Cu(II), and Cd(II) in comparison with other adsorbents.

Adsorbent	Adsorbed	Capacity (mg g ⁻¹)	References
<i>D. dichotoma</i>	Cd(II)	75	[17]
<i>H. clathratus</i>	Cr(III)	7.19	[22]
<i>Pistachio hull powder</i>	Ni(II)	14	[48]
<i>C. barbata</i>		7.30	[22]
<i>Ulva</i>	Cu(II)	250	[49]
<i>Sargassum</i>	Cu(II)	125	[49]
<i>Wheat bran</i>	Cd(III)	21	[50]
<i>Spirulina platensis</i>	Ni(II)	21.3–49.32	[51]
<i>Chlorella vulgar</i>	Ni(II)	18.96–43.89	[51]
<i>Spirulina platensis</i>	Cu(II)	15.01–38.90	[51]
<i>Chlorella vulgar</i>	Cu(II)	12.54–39.10	[51]
<i>Acinetobacter baumannii</i> UCR-2971	Ni(II)	3.5	[52]
<i>Ulva lactuca</i>	Co(II)	0.2406	[53]
<i>H. fusiformis</i>	Cu(II)	42.25	[54]
<i>H. fusiformis</i>	Cd(III)	38.39	[54]
<i>H. fusiformis</i>	Ni(II)	41.87	[54]
<i>E. compressa</i>	Cr(III)	24.99375	Present study
<i>E. compressa</i>	Co(II)	25.06894	Present study
<i>E. compressa</i>	Ni(II)	24.55796	Present study
<i>E. compressa</i>	Cu(II)	24.97502	Present study
<i>E. compressa</i>	Cd(III)	25.3936	Present study

4. Conclusions

In conclusion, this study investigated the potential of *Enteromorpha compressa* macroalgal biomass nanoparticles to act as a biosorbent for removing harmful metals from aqueous solutions. This study revealed valuable insights into the biosorption process through comprehensive characterization and analysis.

The results highlighted the importance of pH in optimizing biosorption efficiency, with a maximum capacity observed at pH 5.0. The fitting of equilibrium data demonstrated that the Freundlich, Temkin, and Langmuir equations provided suitable descriptions of the biosorption process, indicating their applicability in the modeling of metal removal.

Furthermore, this study identified the pseudo-second-order kinetic model as the most accurate in describing biosorption kinetics. The biosorption efficiency was found to increase with rising pH until pH 5, where it reached a maximum level and declined at higher pH values. The correlation between metal cation biosorption and pH was attributed to protonation or deprotonation processes at the biosorbent surface.

The biosorbent dosage showed a slight increase in adsorption capacity up to 50 mg, beyond which no further changes occurred. Higher concentrations of heavy metal ions resulted in improved adsorption capacities, as unoccupied binding sites facilitated the biosorption process.

The biosorption process exhibited a rapid initial adsorption rate, reaching equilibrium within approximately 120 min. The efficiency of *E. compressa* biomass nanoparticles as

biosorbents for removing chromium, cobalt, nickel, copper, and cadmium was underscored by their rapid adsorption rate during the initial phase.

Overall, the experimental data, characterization techniques, and modeling approaches provided a comprehensive understanding of the biosorption performance of *E. compressa* biomass nanoparticles. This study contributes valuable insights into the potential of macroalgal nanoparticle biomass as a sustainable and effective biosorbent for the removal of harmful metals from aqueous solutions.

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